Supporting Information

Reversible phase transitions in a coordination 1D-polymer containing an unusual hexatungstate building block.

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Figure S1. XRPD comparison of the solid bulk of **1** (green lines) *versus* the calculated pattern from single-crystal data of **1** (blue-line).

Figure S2. XRDP comparison of the experimental pattern of the unidentified blue powder obtained during the hydrothermal reaction from the starting reagents (red-line) *versus* the calculated pattern from single-crystal data of compound **1** (green-line) and compound **2** (blue-line).

Figure S3. XRDP comparison of the solid bulk of $\{\{[Cu(OH_2)(bpy)][Cu(bpy)]_2W_6O_{21}\}\cdot 4H_2O\}_n$ (**2**) (blue-line) as obtained from the hydrothermal transformation (180 °C, 7 d) of crystals of **1** *versus* the calculated pattern from single-crystal data of **2** (red-line).

Figure S4. Crystal packing of compound **1** (top) showing the ABAB⋯AB stacking in the *c*-direction of the assembly of molecular decorated clusters *via* intricate π-π and C-H⋯O interactions (bottom). (a) and (b) Distances of the two π-π interactions found in crystal packing of **1**. (c) Representation of the shortest edge-to-face interaction found in the packing of **1**. Interactions (a) and (c) appear through an inversion center of symmetry. Selected intermolecular distances from Cu-centers are also displayed.

Figure S5. Perspective view of the structure of compound **2** along the *a* crystallographic axis showing the *Zipper*-like interdigitation (top) between polymeric chain in the *b*-direction (a, top and b, bottom) and roughly in the *bc*-direction (b, top and a, bottom). The *Zipper*-like intercalations are sustained by π-π interactions (bottom) leading to Cu-Cu lengths shorter than those observed in **1** (shortest Cu-Cu 5.581 in **2** *vs* 5.789 Å in **1**).

Figure S6. TGA of compound **1** (top) and **2** (middle). DSC diagram of compound **2** (bottom).

Figure S7. Nitrogen adsorption/desorption isotherms of compound **2**.

Figure S8. Room temperature EPR spectrum for **2**.

Figure S9. Temperature dependence of the peak to peak linewidth of the EPR spectra. As the behavior of the linewidth when the temperature is increased from r.t. to T= 520 K (247 °C) is indicated by square-points, the triangular-points displays the linewidth when the temperature is decreased abruptly from T= 520 K to r.t. Blue straight-lines distinguish three nearly linear regions.

Figure S10. Temperature dependence of the resonance field obtained from EPR spectra of **2**. The inset shows the variation of g-values in function of the temperature. Square and circles represent the augment and decreasing of T, respectively.

Figure S11. ORTEP representation of the compound **1** (a) and **2** (b).

Figure S12. FTIR spectrum for compound **1**.

Table S1. Crystal data and refinements for crystal structures **1** and **2**.

Table S2. Selected bond distances (Å) for compound **1**.

Table S3. Selected bond angles (°) for compound **1**.

Table S4. Selected bond distances (Å) and angles (°) for compound **2**.

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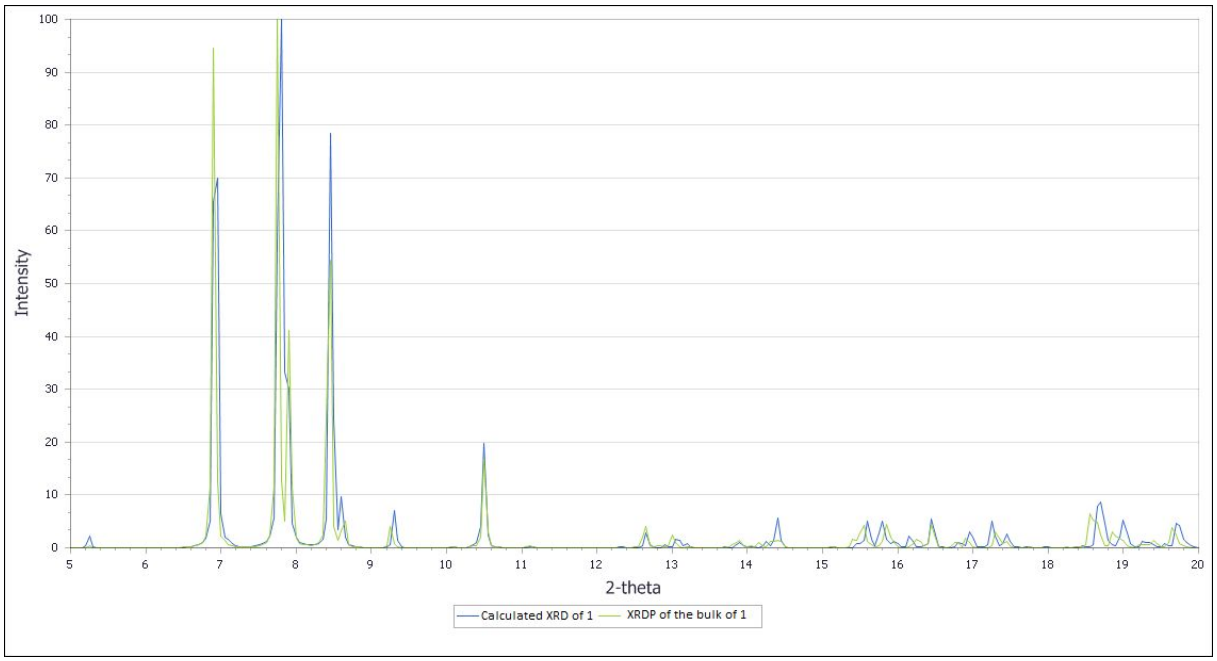

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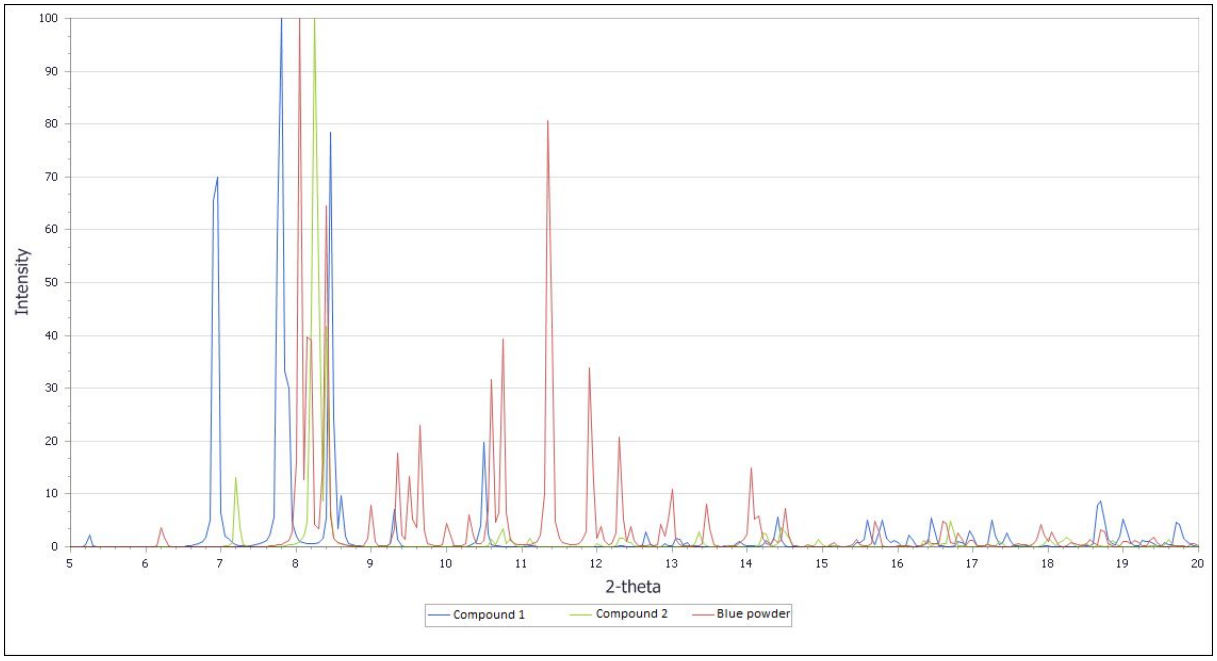

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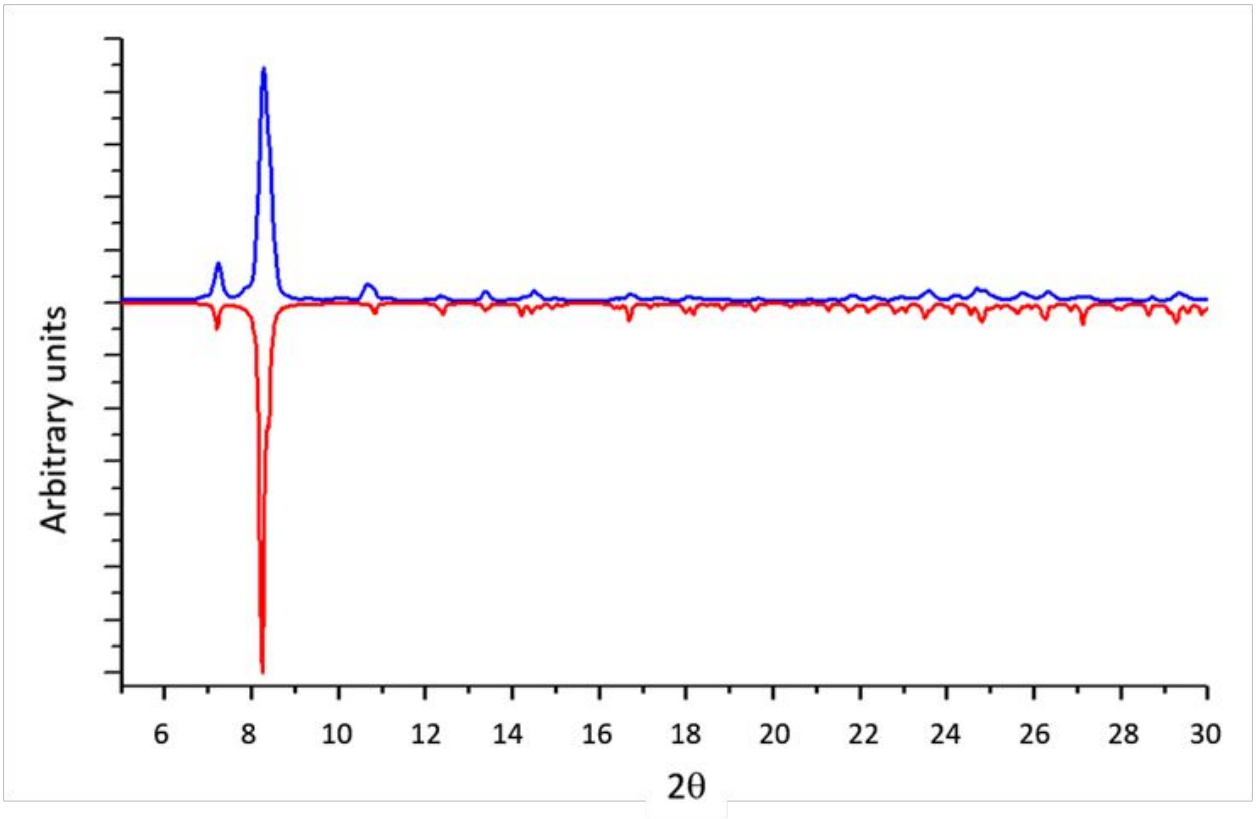

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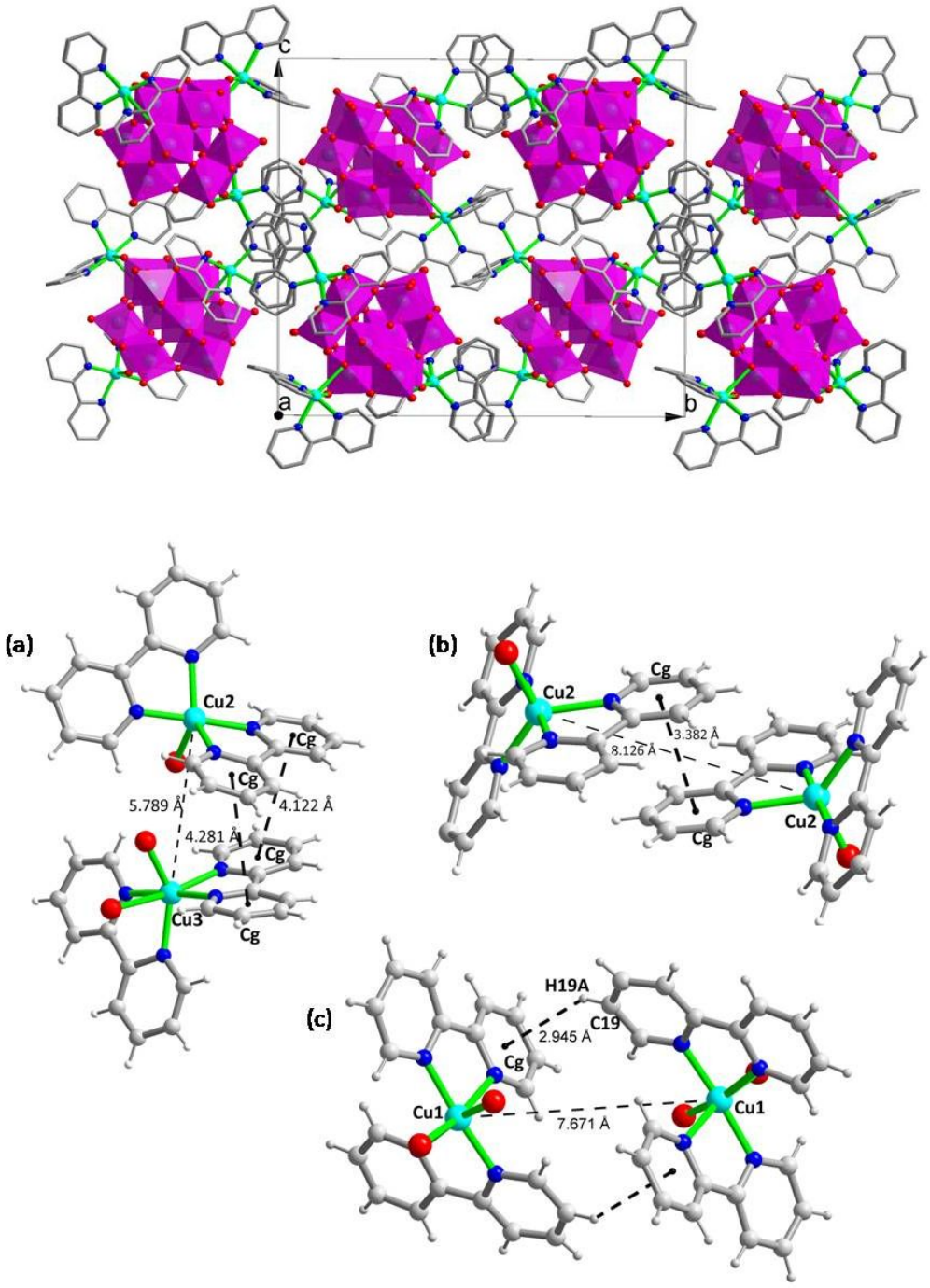

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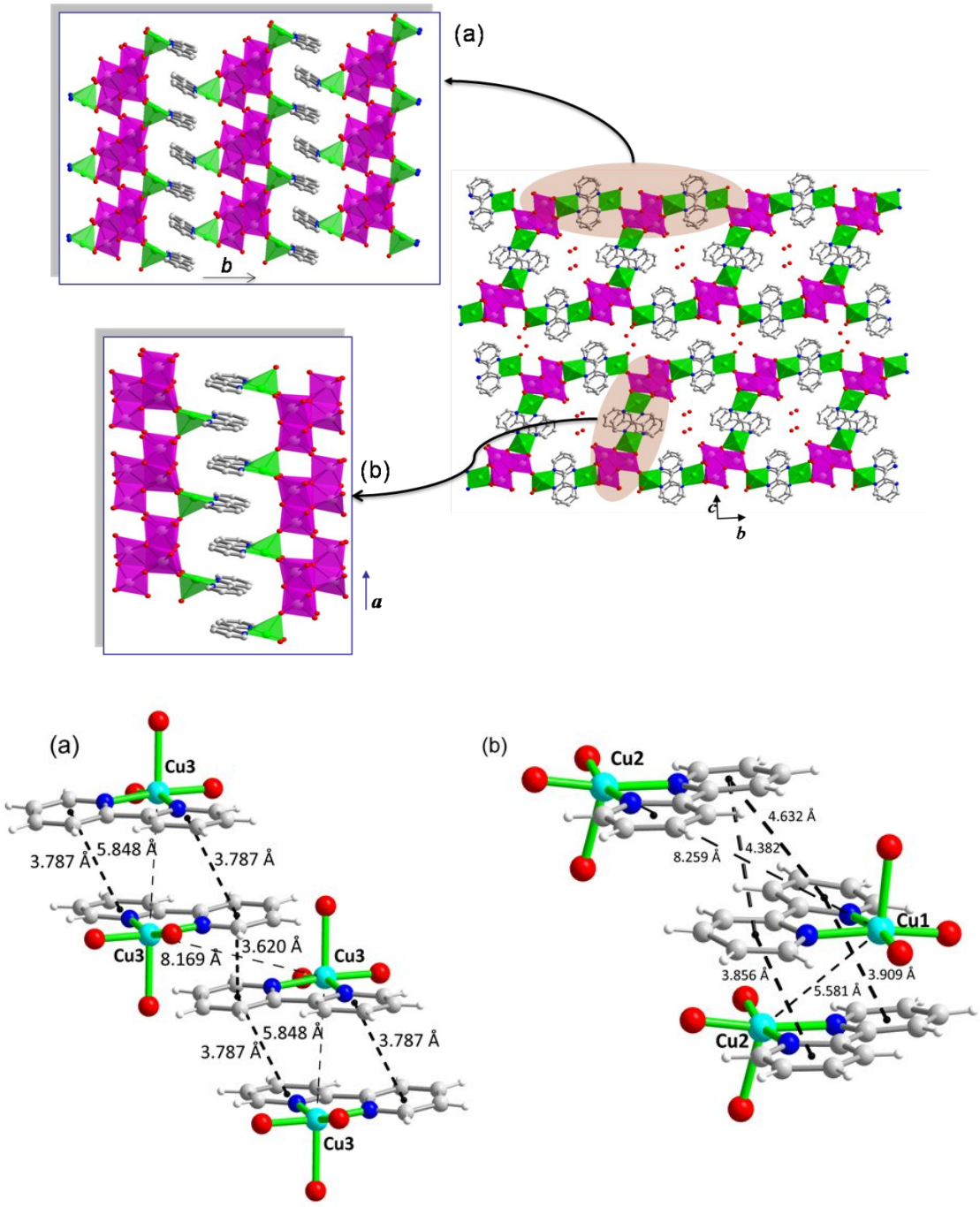

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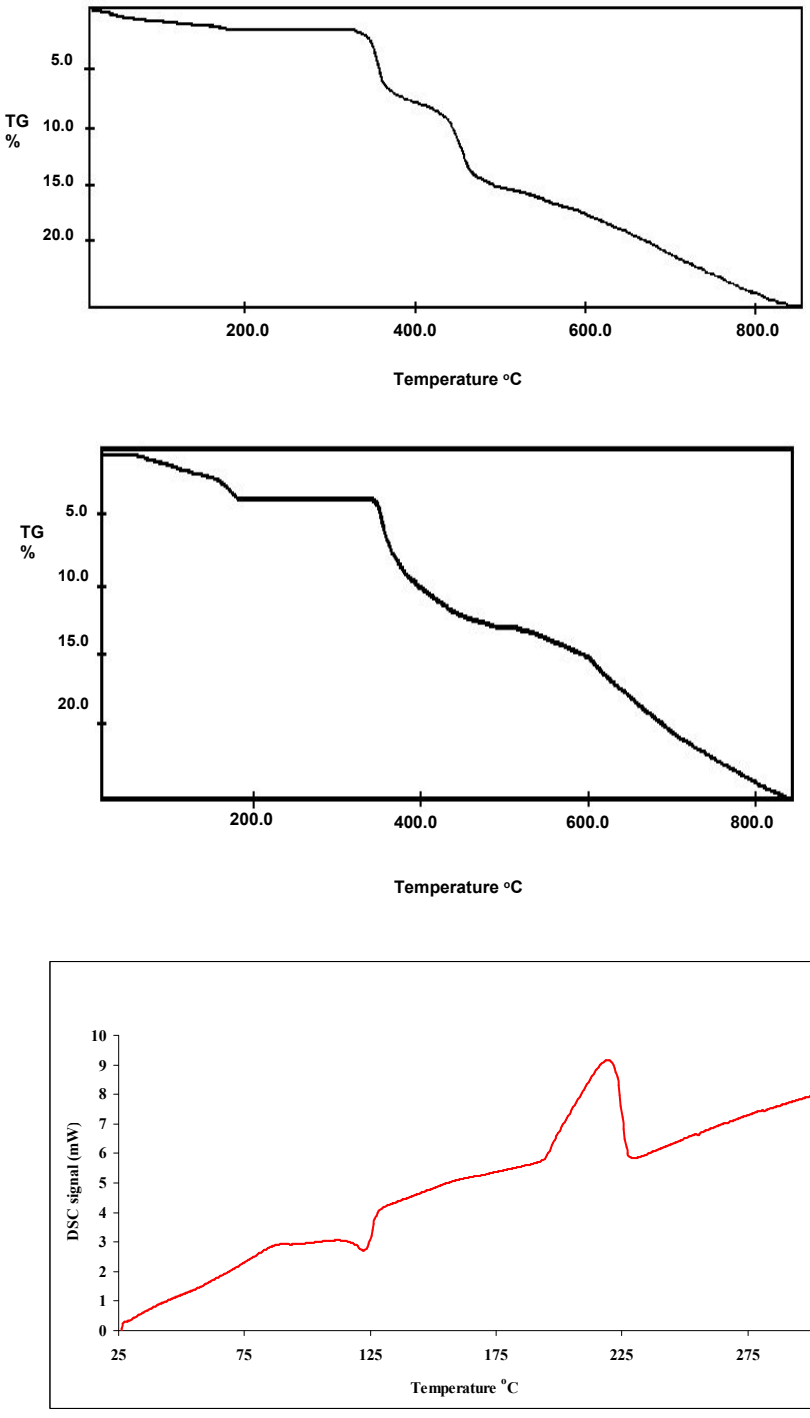


Figure S6. TGA of compound **1** (top) and **2** (middle). DSC diagram of compound **2** (bottom).

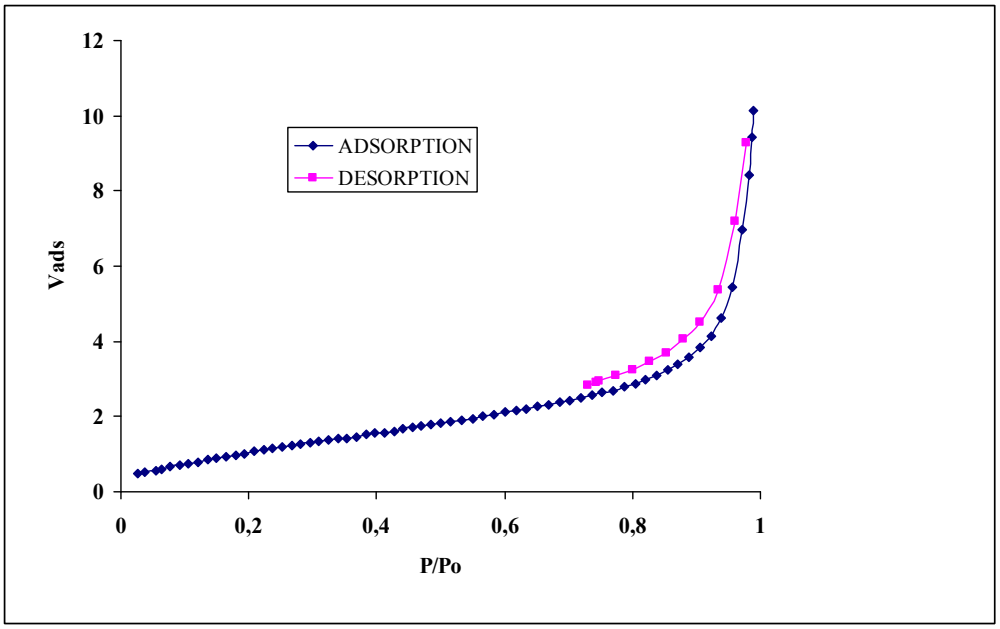


Figure S7. Nitrogen adsorption/desorption isotherms of compound **2**.

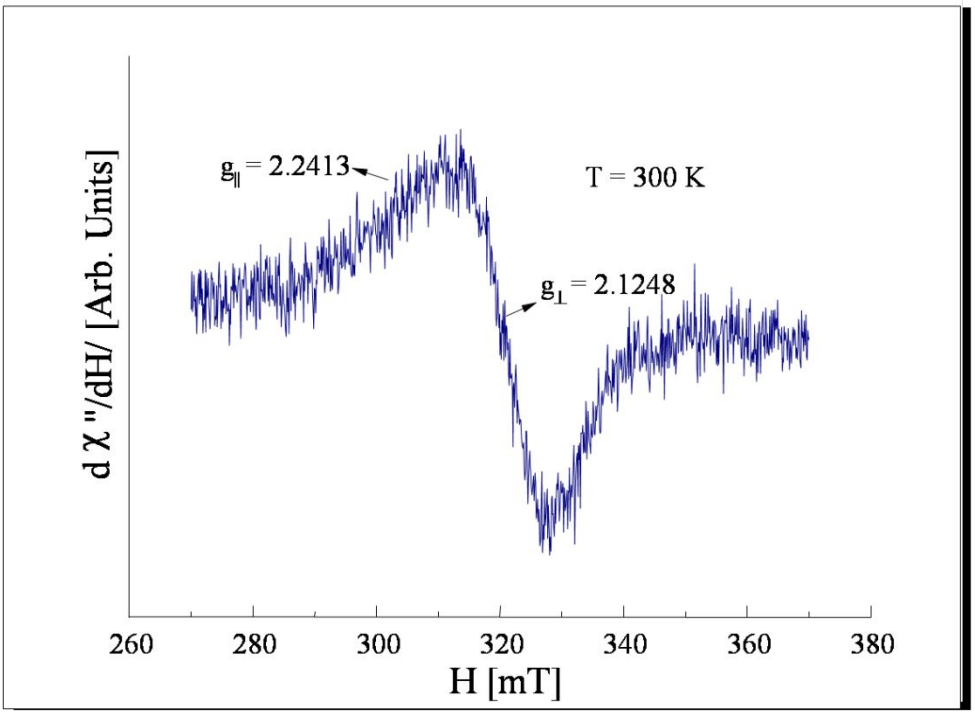


Figure S8. Room temperature EPR spectrum for **2**.

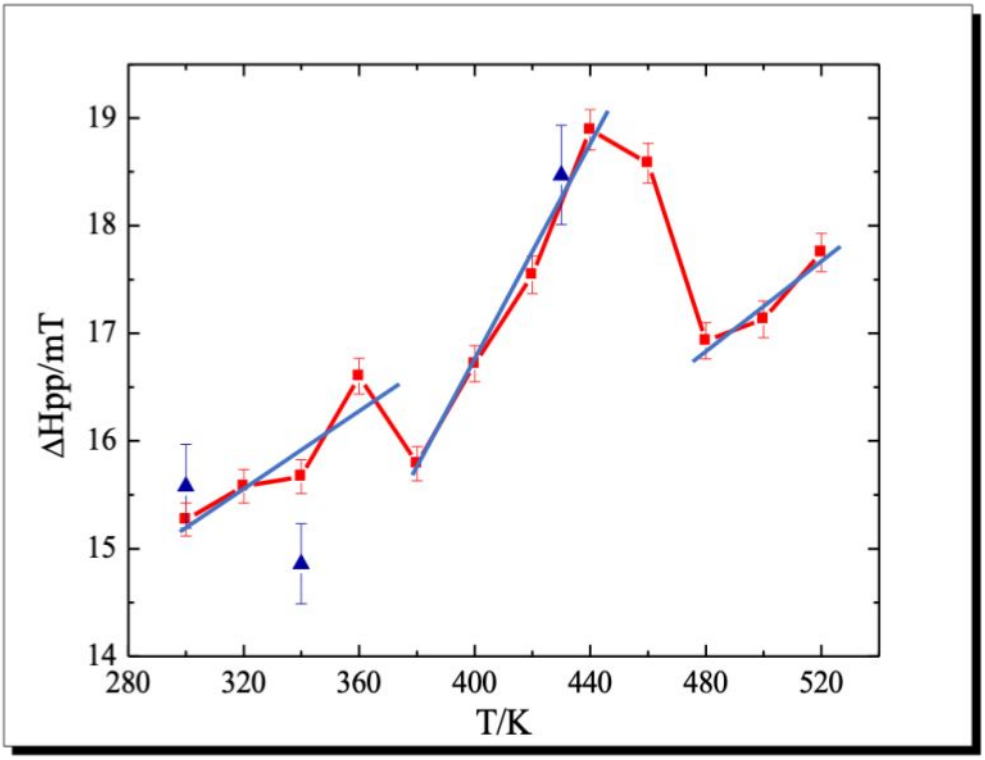


Figure S9. Temperature dependence of the peak to peak linewidth of the EPR spectra. As the behavior of the linewidth when the temperature is increased from r.t. to T= 520 K (247 °C) is indicated by square-points, the triangular-points displays the linewidth when the temperature is decreased abruptly from T= 520 K to r.t. Blue straight-lines distinguish three nearly linear regions.

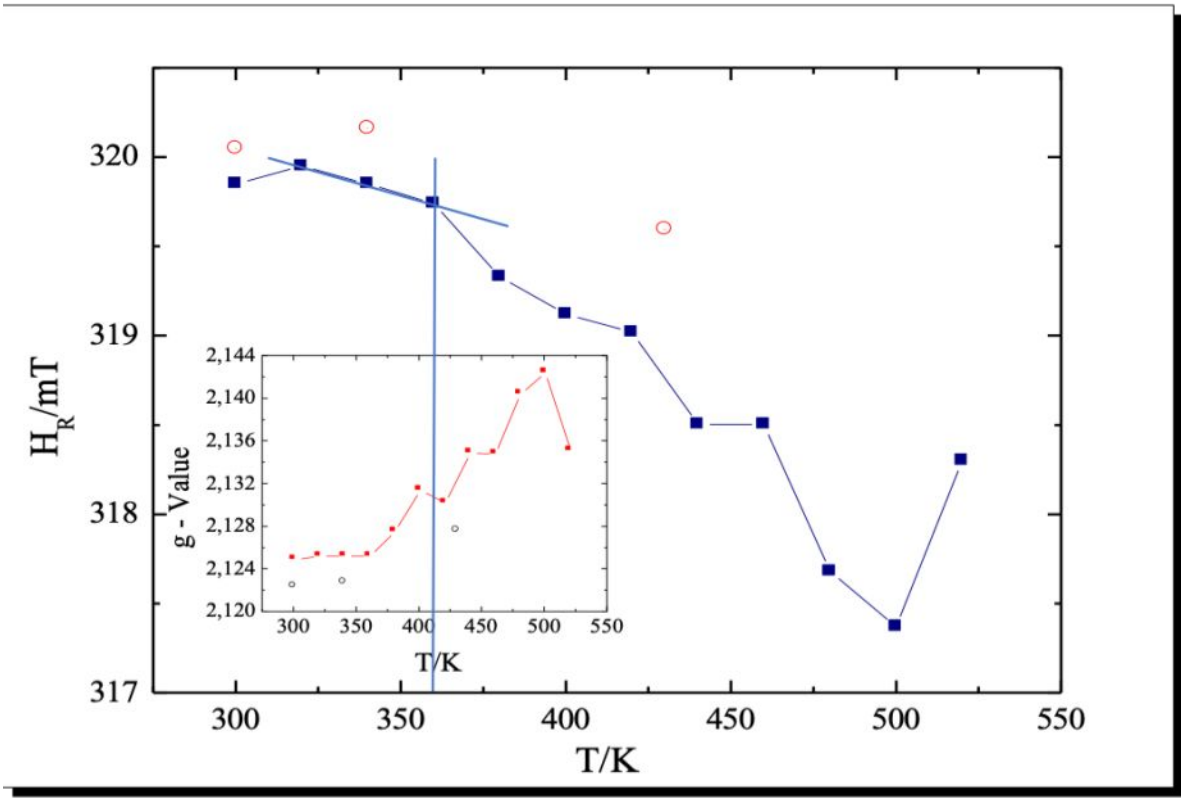
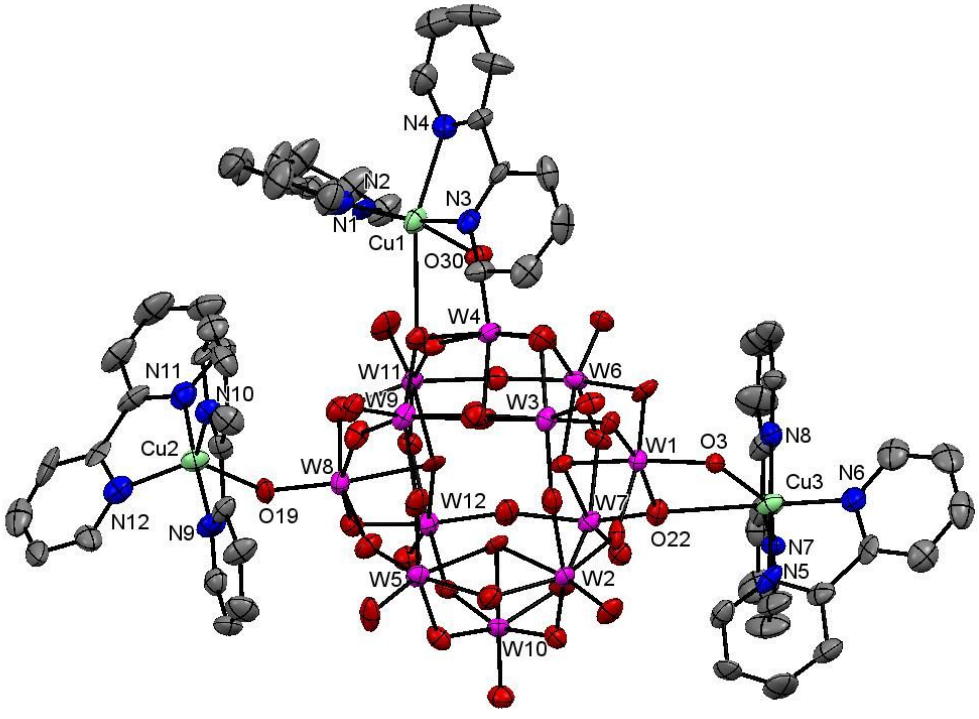
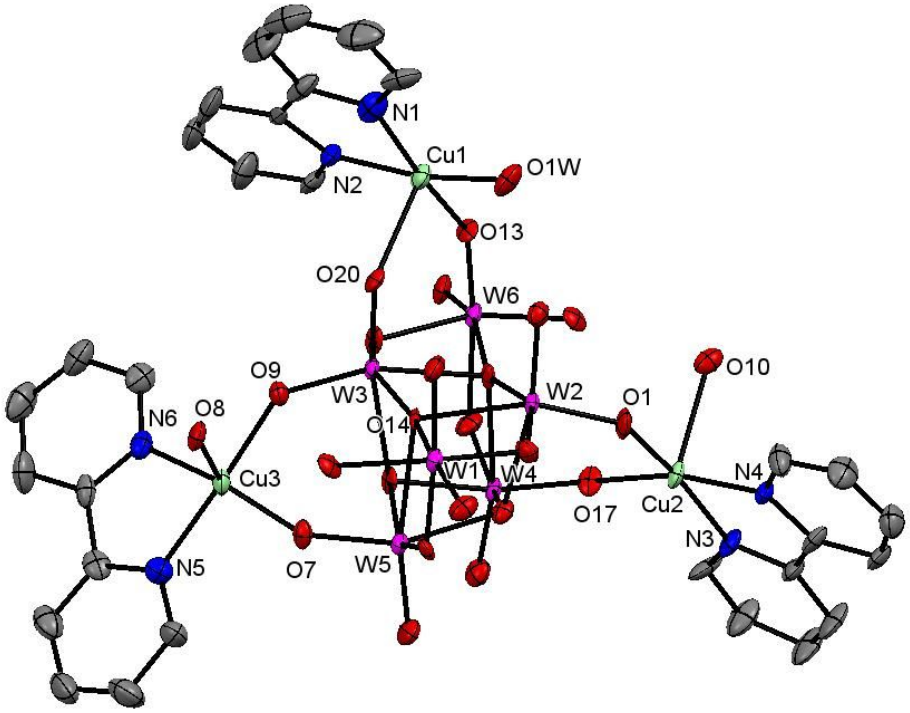


Figure S10. Temperature dependence of the resonance field obtained from EPR spectra of **2**. The inset shows the variation of g-values in function of the temperature. Square and circles represent the increasing and decreasing of T, respectively.



(a)



(b)

Figure S11. ORTEP representation of the compound **1** (a) and **2** (b). Crystallization water molecules and hydrogen atoms are removed for clarity.

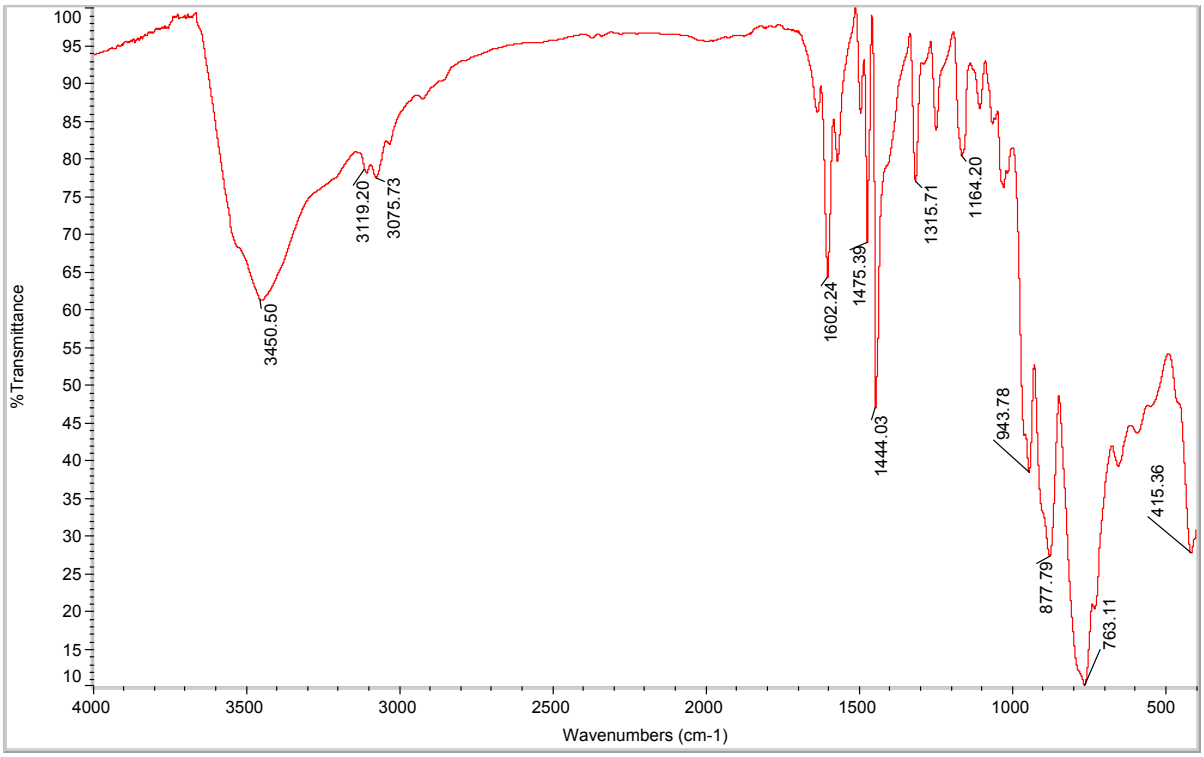


Figure S12. FTIR spectrum for compound **1**.

Table S1. Crystal data and refinement for crystal structures of **1** and **2**.

Crystal data	Compound **1**	Compound **2**
Chemical formula	$C_{60}H_{48}Cu_3N_{12}O_{43}W_{12}$	$C_{30}H_{24}Cu_3N_6O_{26}W_6$
M_r	4021.92	2178.27
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, P(-1)
Temperature (K)	298	298
a, b, c (Å)	14.328(3), 25.528(5), 22.596(5)	8.4859(17), 12.304(3), 21.667(4)
α, β, γ (°)	96.49 (3)	90.60(3), 99.36(3), 94.79(3)
V (Å^3)	8212 (3)	2223.7 (8)
Z	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	17.59	16.95
Crystal size (mm)	0.30 × 0.18 × 0.17	0.22 × 0.12 × 0.04
Data collection		
Diffractometer	Rigaku AFC7S with a Mercury CCD detector	
Absorption correction	Multi-scan Jacobson, R. (1998) Private communication	
T_{min}, T_{max}	0.444, 1.000	0.357, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	86627, 16311, 11650	25852, 8411, 6376
R_{int}	0.074	0.054
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.663	0.662
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.058, 0.130, 1.11	0.056, 0.140, 1.06
No. of reflections	16311	8411
No. of parameters	1161	640
No. of restraints	108	117
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	6.82, −3.40 close to W atoms	3.22, −3.57 close to W atoms

Table S2. Selected bond distances (Å) for compound **1**.

W1—O3	1.778 (10)	W4—O10	2.021 (11)	W8—O33	1.878 (12)	W12—O26	1.722 (12)
W1—O24	1.805 (11)	W4—O31	2.103 (11)	W8—O32	1.929 (12)	W12—O6	1.822 (12)
W1—O21	1.943 (11)	W5—O27	1.683 (11)	W8—O34	1.960 (12)	W12—O7	1.911 (11)
W1—O8	1.947 (12)	W5—O40	1.851 (13)	W8—O25	2.259 (11)	W12—O4	1.933 (11)
W1—O12	2.034 (11)	W5—O37	1.904 (12)	W9—O23	1.700 (11)	W12—O33	1.974 (11)
W1—O22	2.092 (12)	W5—O29	1.931 (12)	W9—O31	1.858 (12)	W12—O25	2.372 (12)
W2—O38	1.690 (11)	W5—O15	1.985 (11)	W9—O32	1.886 (12)	Cu1—N2	1.981 (16)
W2—O18	1.872 (12)	W5—O11	2.321 (11)	W9—O40	1.989 (12)	Cu1—O30	1.989 (12)
W2—O8	1.872 (11)	W6—O20	1.721 (11)	W9—O36	2.016 (12)	Cu1—N3	2.004 (14)
W2—O29	1.926 (12)	W6—O9	1.860 (12)	W9—O10	2.220 (11)	Cu1—N1	2.033 (17)
W2—O5	1.951 (12)	W6—O35	1.881 (12)	W10—O16	1.704 (11)	Cu1—N4	2.241 (17)
W2—O11	2.239 (11)	W6—O21	1.946 (11)	W10—O15	1.881 (11)	Cu2—N9	1.954 (14)
W3—O17	1.721 (12)	W6—O2	2.035 (12)	W10—O7	1.896 (11)	Cu2—N11	1.986 (16)
W3—O36	1.856 (11)	W6—O12	2.249 (10)	W10—O1	1.965 (11)	Cu2—N10	2.051 (14)
W3—O5	1.868 (12)	W7—O14	1.702 (11)	W10—O18	1.984 (12)	Cu2—N12	2.059 (17)
W3—O28	1.954 (12)	W7—O1	1.858 (11)	W10—O11	2.287 (11)	Cu2—O19	2.115 (11)
W3—O24	2.021 (11)	W7—O22	1.867 (12)	W11—O39	1.705 (12)	Cu3—N8	1.983 (15)
W3—O10	2.247 (11)	W7—O6	2.010 (12)	W11—O13	1.872 (12)	Cu3—N5	2.002 (15)
W4—O30	1.789 (11)	W7—O9	2.028 (11)	W11—O4	1.911 (11)	Cu3—N7	2.047 (14)
W4—O2	1.817 (11)	W7—O12	2.189 (10)	W11—O34	1.912 (12)	Cu3—O3	2.051 (11)
W4—O13	1.940 (12)	W8—O19	1.729 (10)	W11—O35	1.941 (11)	Cu3—N6	2.113 (16)
W4—O28	1.940 (12)	W8—O37	1.874 (12)	W11—O25	2.253 (10)		

Table S3. Selected bond angles (°) for compound **1**.

O3—W1—O24	104.0 (5)	O2—W4—O13	89.2 (5)	O1—W7—O6	85.6 (5)	O16—W10—O18	99.1 (5)
O3—W1—O21	92.5 (5)	O30—W4—O28	92.2 (5)	O22—W7—O6	160.6 (5)	O15—W10—O18	87.3 (5)
O24—W1—O21	96.2 (5)	O2—W4—O28	96.5 (5)	O14—W7—O9	93.7 (5)	O7—W10—O18	158.3 (5)
O3—W1—O8	98.6 (5)	O13—W4—O28	166.6 (5)	O1—W7—O9	162.2 (5)	O1—W10—O18	86.2 (5)
O24—W1—O8	88.7 (5)	O30—W4—O10	155.6 (5)	O22—W7—O9	90.4 (5)	O16—W10—O11	167.8 (5)
O21—W1—O8	166.4 (5)	O2—W4—O10	99.1 (5)	O6—W7—O9	82.8 (5)	O15—W10—O11	72.9 (4)
O3—W1—O12	156.8 (4)	O13—W4—O10	88.9 (5)	O14—W7—O12	166.8 (5)	O7—W10—O11	87.7 (4)
O24—W1—O12	98.2 (4)	O28—W4—O10	78.3 (5)	O1—W7—O12	91.3 (5)	O1—W10—O11	84.5 (4)
O21—W1—O12	78.2 (5)	O30—W4—O31	82.2 (5)	O22—W7—O12	75.6 (5)	O18—W10—O11	71.4 (4)
O8—W1—O12	88.6 (4)	O2—W4—O31	171.3 (5)	O6—W7—O12	85.0 (5)	O39—W11—O13	103.7 (6)
O3—W1—O22	84.2 (5)	O13—W4—O31	84.2 (5)	O9—W7—O12	74.3 (4)	O39—W11—O4	99.5 (6)
O24—W1—O22	169.9 (5)	O28—W4—O31	88.8 (5)	O19—W8—O37	102.0 (5)	O13—W11—O4	156.5 (5)
O21—W1—O22	89.2 (5)	O10—W4—O31	75.3 (4)	O19—W8—O33	99.4 (5)	O39—W11—O34	98.5 (6)
O8—W1—O22	84.1 (4)	O27—W5—O40	102.7 (6)	O37—W8—O33	90.9 (5)	N3—Cu1—N1	98.5 (6)
O12—W1—O22	74.6 (4)	O27—W5—O37	101.6 (6)	O19—W8—O32	100.5 (5)	N2—Cu1—N4	94.9 (7)
O38—W2—O18	98.7 (6)	O40—W5—O37	89.0 (5)	O37—W8—O32	86.2 (5)	O30—Cu1—N4	101.0 (5)
O38—W2—O8	102.6 (5)	O27—W5—O29	98.9 (5)	O33—W8—O32	160.0 (5)	N3—Cu1—N4	78.2 (7)
O18—W2—O8	93.3 (5)	O40—W5—O29	92.3 (5)	O19—W8—O34	97.5 (5)	N1—Cu1—N4	92.5 (6)
O38—W2—O29	100.1 (6)	O37—W5—O29	158.7 (5)	O37—W8—O34	160.2 (5)	N9—Cu2—N11	176.2 (6)
O18—W2—O29	89.3 (5)	O27—W5—O15	98.7 (6)	O33—W8—O34	89.6 (5)	N9—Cu2—N10	82.3 (6)
O8—W2—O29	156.5 (5)	O40—W5—O15	158.6 (5)	O32—W8—O34	86.6 (5)	N11—Cu2—N10	98.9 (6)
O38—W2—O5	102.7 (5)	O37—W5—O15	85.6 (5)	O19—W8—O25	168.9 (5)	N9—Cu2—N12	100.3 (7)
O18—W2—O5	158.5 (5)	O29—W5—O15	85.5 (5)	O37—W8—O25	87.8 (5)	N11—Cu2—N12	81.8 (7)
O8—W2—O5	84.1 (5)	O27—W5—O11	165.8 (5)	O33—W8—O25	75.0 (5)	N10—Cu2—N12	130.3 (6)
O29—W2—O5	85.0 (5)	O40—W5—O11	88.6 (5)	O32—W8—O25	85.1 (5)	N9—Cu2—O19	88.0 (5)
O38—W2—O11	170.7 (5)	O37—W5—O11	86.9 (5)	O34—W8—O25	73.1 (4)	N11—Cu2—O19	88.2 (5)
O18—W2—O11	74.5 (5)	O29—W5—O11	71.8 (4)	O23—W9—O31	100.0 (5)	N10—Cu2—O19	122.5 (5)
O8—W2—O11	84.3 (4)	O15—W5—O11	70.5 (4)	O23—W9—O32	102.0 (5)	N12—Cu2—O19	107.2 (5)
O29—W2—O11	73.8 (5)	O20—W6—O9	98.2 (5)	O31—W9—O32	96.6 (5)	N8—Cu3—N5	175.4 (6)
O5—W2—O11	84.0 (4)	O20—W6—O35	100.6 (5)	O23—W9—O40	99.5 (5)	N8—Cu3—N7	81.0 (6)
O17—W3—O36	99.6 (6)	O9—W6—O35	97.0 (5)	O31—W9—O40	159.6 (5)	N5—Cu3—N7	94.5 (6)
O17—W3—O5	102.0 (5)	O20—W6—O21	96.5 (5)	O32—W9—O40	85.3 (5)	N8—Cu3—O3	90.4 (5)
O36—W3—O5	97.6 (5)	O9—W6—O21	93.2 (5)	O23—W9—O36	94.9 (5)	N5—Cu3—O3	92.8 (5)
O17—W3—O28	95.7 (5)	O35—W6—O21	158.6 (5)	O31—W9—O36	90.5 (5)	N7—Cu3—O3	142.5 (5)
O36—W3—O28	92.1 (5)	O20—W6—O2	98.5 (5)	O32—W9—O36	160.2 (5)	N8—Cu3—N6	102.4 (6)
O5—W3—O28	158.0 (5)	O9—W6—O2	163.0 (5)	O40—W9—O36	81.8 (5)	N5—Cu3—N6	80.0 (6)
O17—W3—O24	97.8 (5)	O35—W6—O2	83.0 (5)	O23—W9—O10	167.8 (5)	N7—Cu3—N6	113.3 (6)
O36—W3—O24	162.1 (5)	O21—W6—O2	81.7 (5)	O31—W9—O10	75.7 (4)	O3—Cu3—N6	104.2 (5)
O5—W3—O24	83.0 (5)	O20—W6—O12	167.5 (5)	O32—W9—O10	89.9 (5)		
O28—W3—O24	81.8 (5)	O9—W6—O12	76.1 (4)	O40—W9—O10	84.0 (4)		
O17—W3—O10	167.4 (5)	O35—W6—O12	91.1 (4)	O36—W9—O10	73.9 (4)		
O36—W3—O10	76.2 (5)	O21—W6—O12	73.1 (4)	O16—W10—O15	99.5 (5)		
O5—W3—O10	90.5 (5)	O2—W6—O12	87.0 (4)	O16—W10—O7	102.4 (5)		
O28—W3—O10	72.7 (5)	O14—W7—O1	101.4 (5)	O15—W10—O7	92.3 (5)		
O24—W3—O10	85.8 (4)	O14—W7—O22	99.4 (5)	O16—W10—O1	102.9 (5)		
O30—W4—O2	104.3 (5)	O1—W7—O22	96.1 (5)	O15—W10—O1	157.4 (5)		
O30—W4—O13	98.2 (5)	O14—W7—O6	99.1 (5)	O7—W10—O1	85.9 (5)		

Table S4. Selected bond distances (Å) and angles (°) for compound **2**.

W1—O10	1.724 (9)	W3—O9	1.767 (9)	W5—O12	1.815 (9)	Cu1—N1	2.018 (14)
W1—O19	1.758 (10)	W3—O5	1.853 (9)	W5—O4	2.031 (9)	Cu1—O20	2.275 (9)
W1—O18^{i}	1.920 (9)	W3—O14	1.977 (8)	W5—O21	2.050 (10)	Cu2—O17	1.890 (10)
W1—O6	1.954 (9)	W3—O16	2.192 (9)	W5—O14	2.387 (9)	Cu2—O1	1.948 (11)
W1—O12	2.053 (10)	W3—O4	2.207 (10)	W6—O8	1.734 (9)	Cu2—N4	1.996 (12)
W1—O14	2.483 (8)	W4—O3	1.730 (11)	W6—O13	1.784 (9)	Cu2—N3	2.002 (12)
W2—O15	1.739 (10)	W4—O17	1.778 (10)	W6—O18	1.869 (9)	Cu2—O10^{ii}	2.309 (10)
W2—O1	1.783 (9)	W4—O11	1.835 (9)	W6—O5	2.028 (9)	Cu3—O7	1.885 (9)
W2—O6	1.881 (9)	W4—O21	2.020 (9)	W6—O11	2.037 (9)	Cu3—O9	1.950 (9)
W2—O16	1.985 (9)	W4—O4	2.089 (9)	W6—O16	2.399 (9)	Cu3—N5	1.981 (13)
W2—O14	2.181 (9)	W4—O16	2.368 (10)	Cu1—O13	1.937 (9)	Cu3—N6	2.001 (12)
W2—O21	2.244 (10)	W5—O2	1.723 (10)	Cu1—O1W	1.964 (11)	Cu3—O8^{i}	2.348 (10)
W3—O20	1.746 (9)	W5—O7	1.787 (9)	Cu1—N2	1.989 (13)		

O10—W1—O19	103.3 (5)	O20—W3—O9	103.5 (4)	O2—W5—O7	102.4 (5)	O13—Cu1—O1W	93.4 (4)
O10—W1—O18i	105.0 (4)	O20—W3—O5	97.4 (4)	O2—W5—O12	103.6 (5)	O13—Cu1—N2	94.3 (5)
O19—W1—O18i	92.6 (4)	O9—W3—O5	100.9 (4)	O7—W5—O12	100.7 (4)	O1W—Cu1—N2	169.8 (5)
O10—W1—O6	99.3 (4)	O20—W3—O14	95.9 (4)	O2—W5—O4	105.9 (5)	O13—Cu1—N1	171.0 (4)
O19—W1—O6	94.1 (4)	O9—W3—O14	100.7 (4)	O7—W5—O4	86.1 (4)	O1W—Cu1—N1	90.2 (5)
O18i—W1—O6	152.5 (4)	O5—W3—O14	151.2 (4)	O12—W5—O4	147.4 (4)	N2—Cu1—N1	81.2 (6)
O10—W1—O12	96.0 (4)	O20—W3—O16	96.5 (4)	O2—W5—O21	95.3 (4)	O13—Cu1—O20	92.1 (4)
O19—W1—O12	160.6 (4)	O9—W3—O16	159.9 (4)	O7—W5—O21	155.7 (4)	O1W—Cu1—O20	92.4 (4)
O18i—W1—O12	84.4 (4)	O5—W3—O16	78.0 (4)	O12—W5—O21	90.9 (4)	N2—Cu1—O20	93.9 (4)
O6—W1—O12	80.5 (4)	O14—W3—O16	75.2 (3)	O4—W5—O21	73.1 (4)	N1—Cu1—O20	96.0 (4)
O10—W1—O14	162.9 (4)	O20—W3—O4	169.0 (4)	O2—W5—O14	167.2 (4)	O17—Cu2—O1	91.1 (4)
O19—W1—O14	90.4 (4)	O9—W3—O4	86.1 (4)	O7—W5—O14	90.1 (4)	O17—Cu2—N4	166.8 (5)
O18i—W1—O14	84.3 (3)	O5—W3—O4	85.7 (4)	O12—W5—O14	76.3 (4)	O1—Cu2—N4	94.1 (5)
O6—W1—O14	69.1 (4)	O14—W3—O4	76.9 (4)	O4—W5—O14	71.9 (4)	O17—Cu2—N3	92.4 (5)
O12—W1—O14	70.2 (3)	O16—W3—O4	73.9 (3)	O21—W5—O14	72.0 (3)	O1—Cu2—N3	169.1 (4)
O15—W2—O1	102.8 (5)	O3—W4—O17	103.5 (5)	O8—W6—O13	101.9 (5)	N4—Cu2—N3	80.4 (5)
O15—W2—O6	97.7 (4)	O3—W4—O11	101.8 (4)	O8—W6—O18	104.8 (4)	O17—Cu2—O10^{ii}	94.5 (4)
O1—W2—O6	100.1 (4)	O17—W4—O11	99.8 (4)	O13—W6—O18	98.3 (4)	O1—Cu2—O10^{ii}	87.2 (4)
O15—W2—O16	95.6 (4)	O3—W4—O21	106.7 (4)	O8—W6—O5	96.7 (4)	N4—Cu2—O10^{ii}	97.9 (4)
O1—W2—O16	101.7 (4)	O17—W4—O21	87.2 (4)	O13—W6—O5	87.3 (4)	N3—Cu2—O10^{ii}	102.8 (4)
O6—W2—O16	151.2 (4)	O11—W4—O21	148.2 (4)	O18—W6—O5	156.1 (4)	O7—Cu3—O9	92.2 (4)
O15—W2—O14	98.4 (4)	O3—W4—O4	96.1 (4)	O8—W6—O11	95.5 (4)	O7—Cu3—N5	92.6 (5)
O1—W2—O14	158.8 (4)	O17—W4—O4	155.1 (4)	O13—W6—O11	158.8 (4)	O9—Cu3—N5	172.8 (5)
O6—W2—O14	77.5 (4)	O11—W4—O4	90.8 (4)	O18—W6—O11	88.7 (4)	O7—Cu3—N6	163.4 (5)
O16—W2—O14	75.3 (3)	O21—W4—O4	72.5 (4)	O5—W6—O11	78.8 (4)	O9—Cu3—N6	92.2 (5)
O15—W2—O21	169.2 (4)	O3—W4—O16	168.2 (4)	O8—W6—O16	163.0 (4)	N5—Cu3—N6	81.7 (5)
O1—W2—O21	86.2 (4)	O17—W4—O16	88.3 (4)	O13—W6—O16	88.4 (4)	O7—Cu3—O8^{i}	90.6 (4)
O6—W2—O21	86.3 (4)	O11—W4—O16	76.1 (4)	O18—W6—O16	86.8 (3)	O9—Cu3—O8^{i}	85.1 (4)
O16—W2—O21	76.6 (4)	O21—W4—O16	73.1 (3)	O5—W6—O16	70.0 (3)	N5—Cu3—O8^{i}	100.2 (5)
O14—W2—O21	72.7 (3)	O4—W4—O16	72.4 (3)	O11—W6—O16	72.0 (4)	N6—Cu3—O8^{i}	105.7 (4)

Symmetry codes: (i) $x+1,y,z$; (ii) $x-1, y, z$.